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GIFFORD PINCHOT, Forester.

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# THE ANALYSIS AND GRADING OF CREOSOTES.

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## THE ANALYSIS AND GRADING OF CREOSOTES.

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### INTRODUCTION.

Since the publication of Forest Service Circular 80, "The Fractional Distillation of Coal-tar Creosote," laboratory work on the composition of creosotes has been continued and a considerable quantity of data has been gathered. The Forest Service has been greatly helped by the numerous criticisms and suggestions which were offered regarding the work described in Circular 80. The most important of these is that in the previous work no corrections were made for variations in thermometer readings due to the emergent stem, a criticism which has this much weight—that very considerable variations will arise if the number of degrees on the emergent portion of the stem is different in different analyses, or if the correction is made for this emergent stem in some cases and not in others.

### EMERGENT THERMOMETER STEM CORRECTIONS.

The formula commonly used for this correction is  $0.00016 (T-t)N$ , in which  $T$  equals the thermometer reading,  $t$  the temperature of the emergent stem, and  $N$  the number of degrees of the thermometer reading which are exposed. If, therefore, the thermometer reading is  $300^{\circ}$ ,<sup>a</sup> the temperature of the emergent stem is  $50^{\circ}$ , and the first number on the stem which appears above the cork is  $200^{\circ}$ , the correction would be  $0.000016 \times 250 \times 100 = 4.0^{\circ}$ . At any given thermometer reading the most important factor in the correction will be  $N$ , which means that with the thermometer placed so that the same degree is at the surface of the cork in every case the variation in the correction to be applied will be very small. At any given thermometer reading with the same kind of apparatus, the variation in the temperature of the emergent stem,  $t$ , is small, not over  $10^{\circ}$ . A difference of  $10^{\circ}$  in  $t$  would produce only a slight variation in the final result. In the example given above, if the temperature of the emergent stem had been  $60^{\circ}$  instead of  $50^{\circ}$ , the correction would have been  $3.84^{\circ}$  instead of

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<sup>a</sup> All thermometer readings in this circular refer to the centigrade scale.

4.0°, a difference of only 0.16°. Consequently, if the thermometer is always placed so that the same point is at the surface of the cork, the results will be constant within the limits of error in the methods employed.

In making the distillations, the curves of which are shown in figures 8 to 14 in Circular 80<sup>a</sup> and in the various figures in this circular, the thermometer was placed so that the first reading above the cork was 200°. The corrections which should be applied to these curves are given in Table 1.

TABLE 1.—*Corrections for the emergent thermometer stem.*

Temperature reading.	Stem temperature.	Degrees emergent.	Correction.	Corrected reading.	Temperature reading.	Stem temperature.	Degrees emergent.	Correction.	Corrected reading.
170	-----	0	0	170	250	48.5	50	1.6	251.6
180	-----	0	0	180	260	50	60	2	262
190	-----	0	0	190	270	52	70	2.4	272.4
200	-----	0	0	200	280	53.5	80	2.9	282.9
210	42	10	0.3	210.3	290	55	90	3.4	293.4
220	43.5	20	0.6	220.6	300	57	100	3.9	303.9
230	45	30	0.9	230.9	310	58.5	110	4.4	314.4
240	47	40	1.2	241.2	320	60	120	5	325

It is important in describing any method for creosote analysis that the number of degrees which shall appear on the emergent stem be specified. If this specified position of the thermometer is adhered to variations arising from the emergent stem will be insignificant.

#### THE GRADING OF CREOSOTES.

At the present time, so long as creosote oils conform to certain specifications, which are usually liberal, they bring the same price. As a matter of fact, the different creosotes have different values and are not equally fitted for the same purposes. For example, an oil which might be admirably adapted to methods of treatment in which it is not exposed for any considerable time might be so volatile that in methods in which it is exposed the waste would be excessive; or, again, an oil to be used for wood which is to be placed under ground, such as the conduit pipes for telephone lines, would be unfitted for purposes where the timbers would be exposed to heat and changes of air, conditions allowing a maximum volatilization. Further than that, the tars obtained from other sources than the carbonization of coal are being distilled, and the oils obtained in this way are being used, either alone or mixed with coal-tar creosote, for the preservation of timber.

<sup>a</sup> The statement regarding thermometer corrections on p. 26 of Circular 80 was not as precise as it should have been; the corrections given there are those required when the first emergent reading was 170°, as was the case in the earlier distillations from a 200 c. c. flask.

Our present knowledge of the values of the different oils is too meager to permit as accurate grading as would be desirable, but sufficient experimental data and practical experience have been accumulated to lay the foundations for such a system of grading. A first-quality creosote oil should be one which may be easily introduced into the wood with a minimum loss in the process, and which, when once there, will stay and efficiently protect the timber. In other words, a high grade creosote must have properties which render its diffusion through the wood easy, and is further characterized by a minimum content of low-boiling oils and by qualities which enable the treated timber to offer the greatest resistance to fungi and boring insects.

Although it is true that the most important factors which affect penetration are not those arising from the character of the oil, but depend more upon the species of the wood, its relative quantities of heart and sap wood, its moisture content, and the manipulation of temperatures and pressures during the treating process, nevertheless, the character of the oil is not without influence. The two significant properties of creosote are its viscosity and the presence of free carbon. With pure coal-tar distillates the viscosity is practically constant and there should be no appreciable quantity of free carbon.

The loss from volatilization during the treating process will depend upon the methods used and upon the character of the oil; and after the timber is treated, the loss by vaporization will be governed by the character of the oil and the situation in which the treated wood is placed. The factors which influence the volatility of a creosote are its water content and the amounts of low-boiling oils and of naphthalene. The water is doubly responsible, since not only is it very volatile itself, but its evaporation increases the volatilization of the other creosote constituents. Although naphthalene is a rather high-boiling compound, its great volatility at low temperatures is well known. It is on this account that the loss due to the high content of naphthalene is greater than would be expected from an oil with so high a boiling range as creosote.

The resistance which treated timber offers to attacks of fungi and borers depends upon both the physical and the chemical properties conferred by the treatment. Of the physical properties the most important one is the permeability of the wood to water. If a perfectly dry timber were so treated that water could not enter it its life would be assured. Unfortunately, creosoting does not result in completely waterproofing wood, and no data are available regarding the degree of permeability of wood treated with different sorts of oil.

The important chemical properties of a creosote which fit it to be a preservative are those which increase its toxic qualities toward fungi



and wood-destroying insects. Although there are exceptions, it is a general rule that the compounds belonging to the aromatic series are more poisonous to both plants and animals than those in the paraffin and olefin series, and that the former are consequently of much greater antiseptic value. A pure coal-tar creosote will protect properly treated timber for a great many years. What protection will be afforded by the distillates from other kinds of tar is as yet an open question, but the increased production of these tars and the growing practice of distilling them make it imperative that definite information regarding their preservative value should be acquired. At present, despite the apparent approximation to the composition of coal-tar creosotes by the creosotes from oil or water-gas tars, the known preservative value of the pure coal-tar creosotes makes them of greater market value. We must, therefore, regard the creosotes obtained by the distillation of properly made coal tars as the highest grades for preservation. It is, of course, well known that by varying the conditions under which coal is decomposed tars are obtained which differ in composition. With distillations at low temperatures the production of aromatic compounds is reduced, and the resulting tar contains compounds analogous to those present in crude petroleum; hence the single specification that a creosote shall be distilled from pure coal tar does not necessarily assure a high-grade oil. In addition to being a pure distillate from coal tar, the creosote must also possess a composition which gives it properties falling within narrow limits.

#### EXPERIMENTAL DATA.

##### VOLATILITY OF CREOSOTES.

The losses of creosote from its volatility have received scant attention. These losses may occur from the creosote itself before and during treatment or from the creosoted timbers. Some methods of treatment entail an excessive loss when highly volatile oils are employed, oils which would be well enough adapted for processes which entail only a small degree of exposure of the oil.

This point has been emphasized in some of the experimental treatments conducted by the Forest Service. A number of telephone poles, the seasoning of which had been the subject of investigation, were given butt treatments by an open-tank process. The butts of the poles were placed in tanks of hot creosote, which was kept for several hours at from 2° to 10° above the boiling point of water. The fires were then drawn and the oil allowed to cool with the poles remaining in it. As the oil was taken up by the timber fresh oil was added. A sample of the creosote just as it came from the barrels and a sample

of the oils remaining in the tank at the end of the treatments were sent to the laboratory for analysis. The curves shown in figure 1 give the results of the fractional distillations.

The distillations were made from ordinary 500 c. c. distilling flasks.

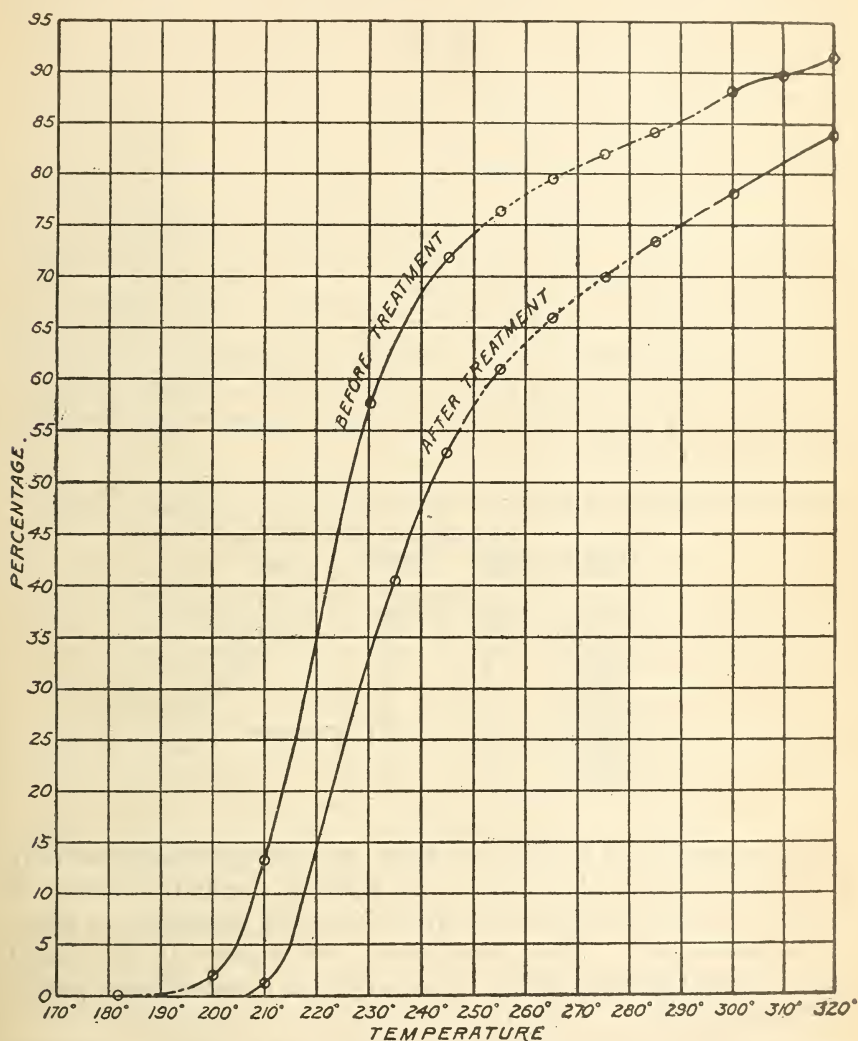


FIG. 1.—Distillations of creosote 46 before use in open-tank treatment, and the same creosote (No. 47) after use.

The kinds of lines used in the curves represent the consistencies of the various parts of the distillate. Solid lines represent fractions solidifying on cooling, dotted lines show liquid fractions, dashed lines represent a pasty consistency, and dashes interspersed with varying num-

bers of dots show varying conditions from the semisolid to liquids with a few floating crystals.<sup>1</sup> The loss of certain portions of the oil during the treatment is obvious; for example, the original oil yielded 13 per cent of distillate below 210°, whereas the oil after treating operations gave but 1 per cent. Calculation shows that, assuming that there was no loss of the portions of the oil which distill above 245°, it would require 1.7 gallons of the original oil to furnish the amount of distillate above 245° which is obtained from 1 gallon of the residual oil. This indicates a loss of 41 per cent of the total creosote. A record was kept of the amount of oil put into the tanks and of the amounts absorbed by the poles, as shown by weighings before and after treatment, making allowance for the moisture lost during the process. The results showed a discrepancy of over 38 per cent between the oil used and that finally gotten into the timbers.

It is interesting to compare the weights of the various fractions of the residual and original oils if, instead of equal amounts for each distillation, 59 per cent as much of the residual oil were used as of the original. The distillations would then represent equal quantities of the original creosote.

TABLE 2.—*Localization of loss by evaporation of creosote during treatment.*

Tempera- tures.	Original oil.	Residual oil.	Loss.
<i>Degrees.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
210	13.0	0.6	12.4
210-235	50.5	23.2	27.3
235-245	8.5	7.3	1.2
245-255	4.7	4.8	} Duplicates.
255-265	3.2	2.9	
265-275	2.2	2.3	
275-285	2.3	2.1	
285-300	3.9	3.8	
300-320	3.6	3.6	
Residue.	8.1	9.1	

Table 2 shows that in the case of this oil the loss is almost entirely in the part distilling below 235°. In figure 2, distillation curves of another oil are given, before and after open-tank treatments of chestnut telephone poles. These distillations were made with the special flask described on page 30, by means of which a better fractionation is effected.

Laboratory tests of volatility were made on a number of creosotes. Five cubic centimeters of each melted oil were measured into tared glass crystallizing dishes 67 mm. in diameter. After the oil had cooled each dish with its contents was weighed and then kept for four hours at a temperature of 98°. Then they were cooled and weighed again, and the percentage losses calculated. These are shown in Table 3.

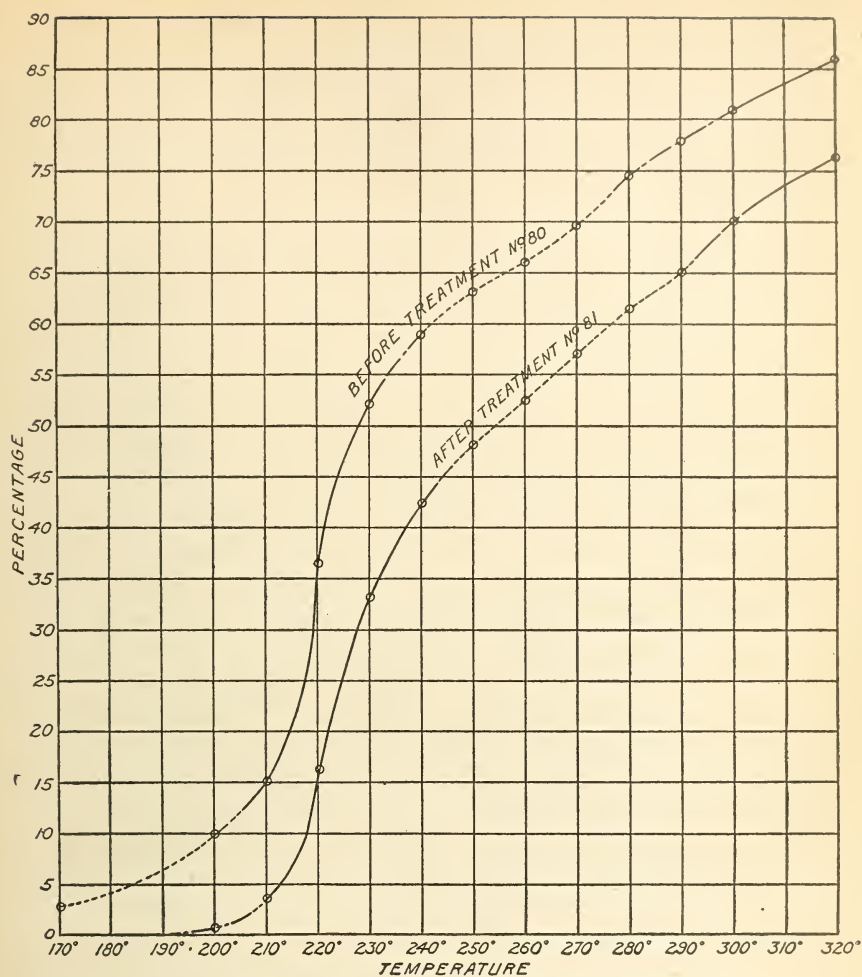


FIG. 2.—Distillations of creosote 80 before use in open-tank treatment, and the same creosote (No. 81) after use.

TABLE 3.—Comparative volatilities of creosotes at 98°.

Creosote No.	Loss.	Temperature at which same loss will be secured during distillation.	Creosote No.	Loss.	Temperature at which same loss will be secured during distillation.
	<i>Per cent.</i>	<i>Degrees.</i>		<i>Per cent.</i>	<i>Degrees.</i>
13	42.2	260	41	80.6	245-250
14	51.1	235-240	42	53.6	230-235
15	56.4	235-240	43	24.6	255-260
40	63.7	240-250	46	71.7	240-245



The distillation curves of several of these oils are given in Circular 80; No. 13 on pages 13 and 21, 14 on page 22, 15 on page 23, 41 on page 26, and 42 on page 27. No. 46 is the oil before use in the open-tank treatments mentioned on page 8 of this circular, and shown in figure 1. No. 40 is shown in figure 6, and 43 in figure 3, of this circular.

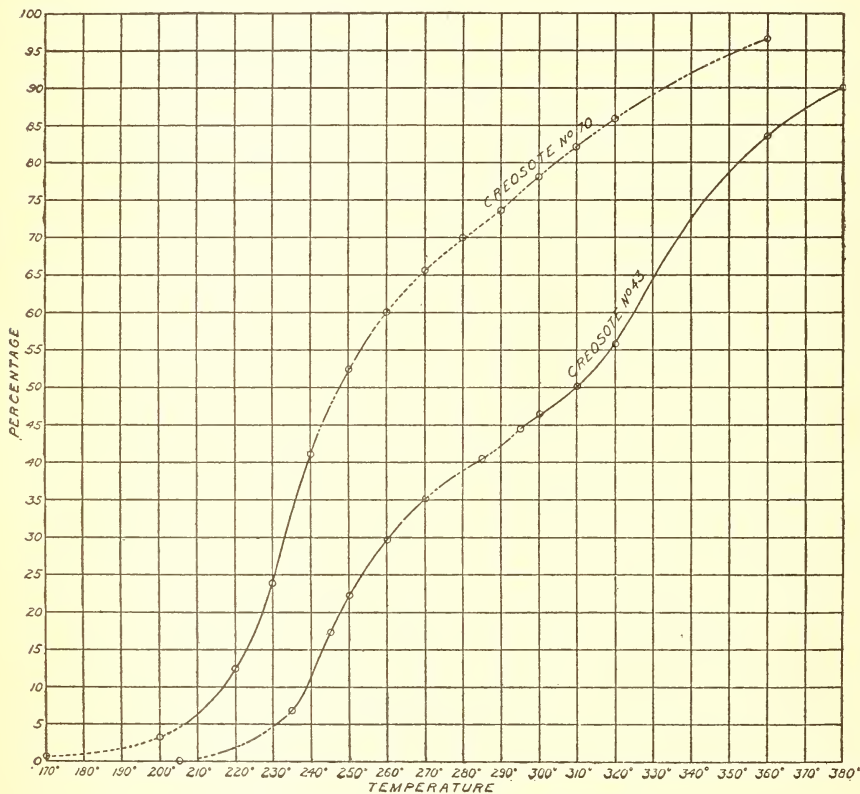


FIG. 3.—Distillation of creosotes 43 and 70.

A second series of tests was made in which the volatilization was determined for lower temperatures. The results are given in Table 4. The periods and temperatures were (1) four hours at 60°, followed by (2) ninety hours at 20°, followed by (3) five hours at 60°, followed by (4) forty-five hours at 20°, followed by (5) two weeks at 20°.



TABLE 4.—*Comparative volatilities of creosotes at low temperatures.*

Creosote.	Loss—						Temperature at which same loss will be secured during distillation.
	4 hours at 60°.	90 hours at 20°.	5 hours at 60°.	45 hours at 20°.	2 weeks at 20°.	Total.	
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Degrees.</i>
51	37.2	4.1	18.3	0.6	3.2	62.8	246
41	41.9	4.2	24.9	.8	3.6	74.6	239
46	30.1	4.0	25.1	1.4	7.2	66.5	238
47	20.2	3.6	18.7	1.8	6.4	49.0	241
15	31.0	4.2	23.8	.8	4.6	63.7	237
43	14.1	2.3	8.7	.9	3.1	28.3	261
70	27.3	4.7	18.3	1.2	4.6	55.0	252

No. 51 is a rather low-boiling creosote from a coke-oven tar; No. 47 is the oil remaining after the open-tank treatments shown in figure 1; No. 70 was prepared in the laboratory from a water-gas carburetor tar, and its distillation curve is shown in figure 3.

From the results given in Table 4, it is evident that creosotes vary greatly in their volatility and that the differences are most marked at the higher temperatures around the boiling point of water. The relative volatility may be judged from the results of a fractional distillation, although the high-boiling oils lose rather more than would be expected.

Not only do the creosotes themselves vary in volatility, they also show marked differences after they are injected into wood. In tests on creosoted blocks, creosote No. 15 evaporated from wood at nearly twice the rate of No. 43. (Compare Table 3.) Exposure of treated timbers to an abundant air circulation, and to some heat, affects the loss by volatilization to a marked degree. This fact was brought out by analyses of the wood from different portions of a creosoted telephone pole in the Norfolk to Washington line of the American Telephone and Telegraph Company. This pole had been in service for about nine years. The creosote was extracted from samples obtained by making 1-inch borings in three different portions of the pole: first, centered 1 inch from the outside of the underground portion; second, centered 1 inch from the southern side of the pole near the cross-arm; and third, centered 3½ inches from the outside of the pole in the cross-arm region. The creosotes extracted from these three localities were fractioned from a 200 c. c. distilling flask, with the results plotted in figure 4.

If the average distillation of the creosote used in treating the poles in this line, as given by the analyses made in the laboratory of the American Telephone and Telegraph Company, were plotted on the

same sheet, it would almost coincide with the curve for the oil extracted from the butt.

#### PROPERTIES OF PURE COAL-TAR CREOSOTE.

The composition of pure coal-tar creosote is subject to considerable variation, due to the character of the coal used and to the methods

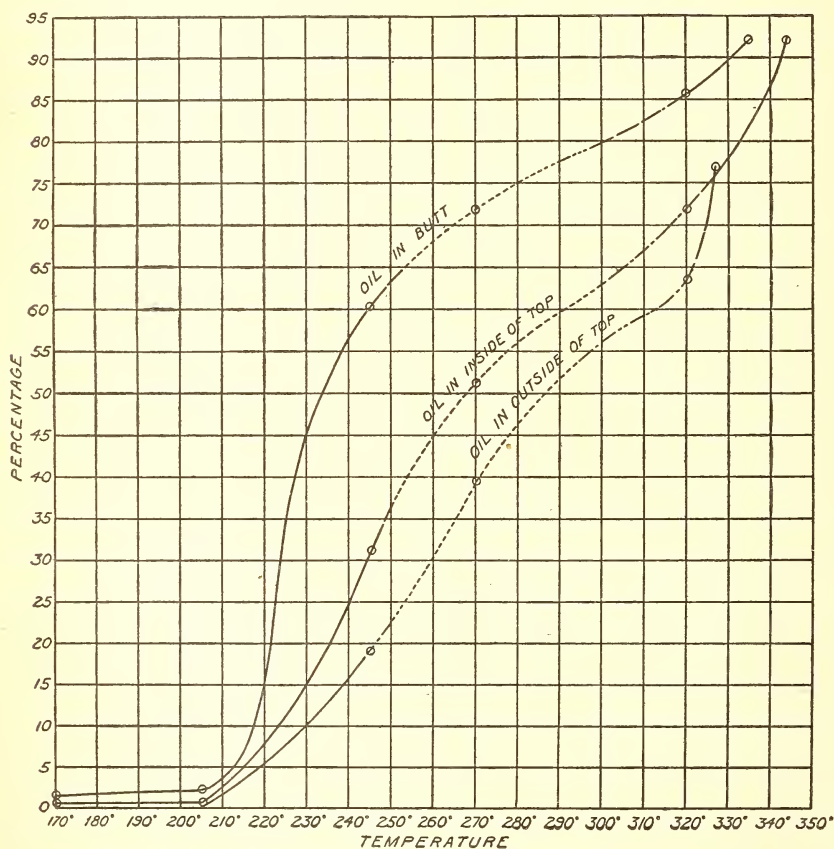


FIG. 4.—Distillations of creosote extracted from different portions of a treated telephone pole.

of carbonization. It is on account of these variations that it is a matter of some difficulty to detect the presence of oils distilled from other kinds of tar when mixed with a product from coal tar. Although it is possible to obtain, from the distillation of coal, creosotes of markedly different properties from those ordinarily produced, yet the conditions of carbonization which are ordinarily employed yield

creosotes with properties which fall within very limited ranges. These creosotes contain maximum quantities of aromatic compounds, and, as far as our present knowledge extends, they may be regarded as the best type for timber preservation.

Various chemical tests have been tried to distinguish creosotes made from tars of other materials than coal. So far only one of these, the sulphonation test, has proved satisfactory. The most constant properties of the coal-tar creosotes are certain physical constants of the fractions obtained by a careful fractional distillation. Of these, the index of refraction and the specific gravity are most serviceable.

In working out the range of these physical properties some commercial creosotes were used and some creosotes prepared from

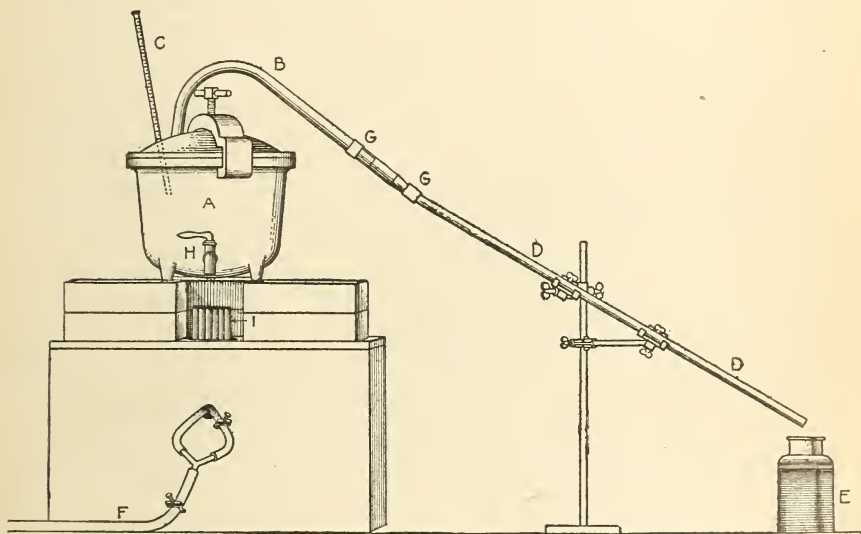


FIG. 5.—Apparatus used for preparing creosotes from tar.

authentic samples of tar. The results obtained by a study of the physical properties of the distillates from creosotes of known purity were compared with the data obtained by a similar study of other oils, some of which were distilled from tars in the laboratory. In preparing creosotes from tar, a 2-gallon iron still was used. (Fig. 5.)

The distillate was rejected up to the point where it had a specific gravity greater than that of water, and the heavy distillate was collected from that point until the residue in the still was either a soft or hard pitch.

In making fractional distillations of the various oils, 250 grams of creosote were distilled from a 500 c. c. distilling flask and a large number of separate fractions collected.

## INDEX OF REFRACTION.

The index of refraction is the ratio between the sines of the angles of incidence and of refraction of light, expressed by the formula  $n = \frac{\sin I}{\sin R}$ , where  $n$  means the index of refraction referred to sodium light,  $I$  equals the angle of incidence, and  $R$  the angle of refraction. The index of refraction varies with the temperature, but is constant for any given oil at a stated temperature. In making measurements of the index of refraction of the different fractions of a creosote distillation, it was necessary to make the measurements at 60°. The

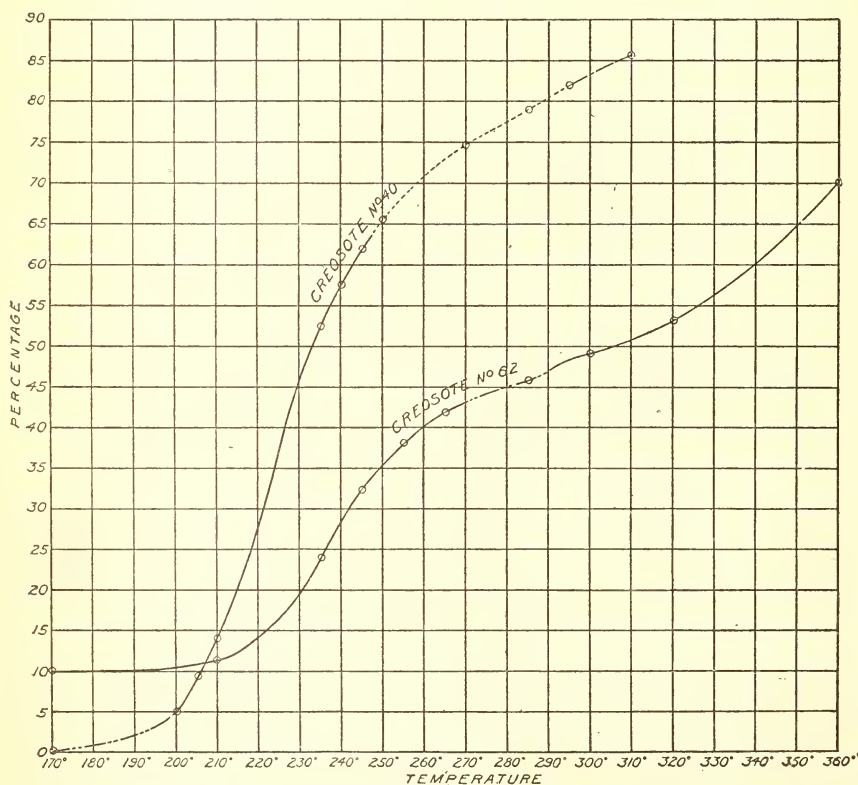


FIG. 6.—Distillation of creosotes 40 and 62.

determinations were made with an Abbe refractometer provided with a light compensator. By means of this instrument the index of refraction may be read with great accuracy, and the measurement is one of the most exact which can be applied to such an oil.

The distillations and the indices of refraction of two very different oils, Nos. 40 and 62, are shown in figures 6 and 7. As shown by the distillations, No. 40 is a rather light, low-boiling creosote, and No. 62 one of the extremely heavy tar oils.



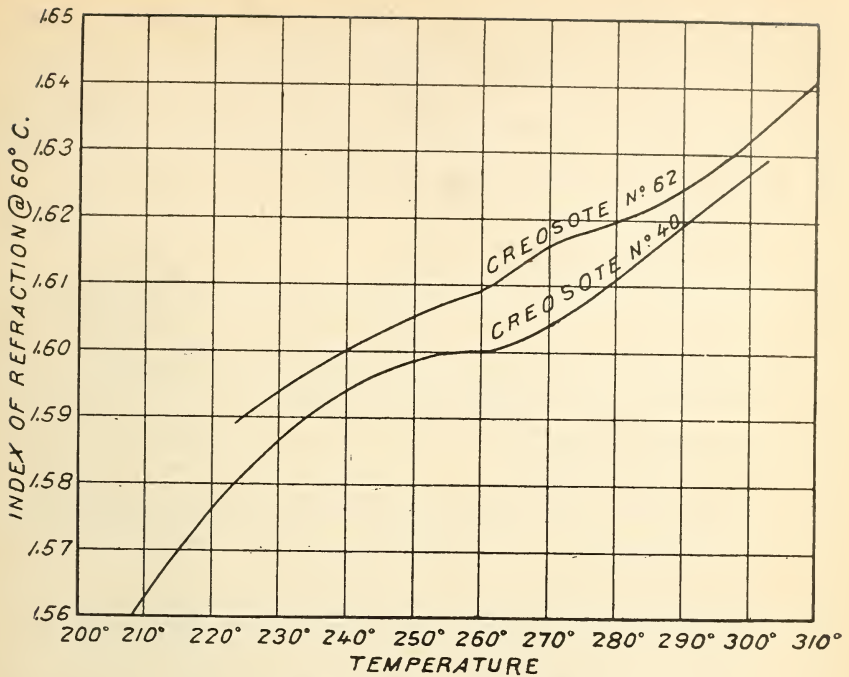


FIG. 7.—Indices of refraction of creosotes 40 and 62.

In figure 8 is given the range of index of refraction within which have fallen all the creosotes the purity of which was without question.

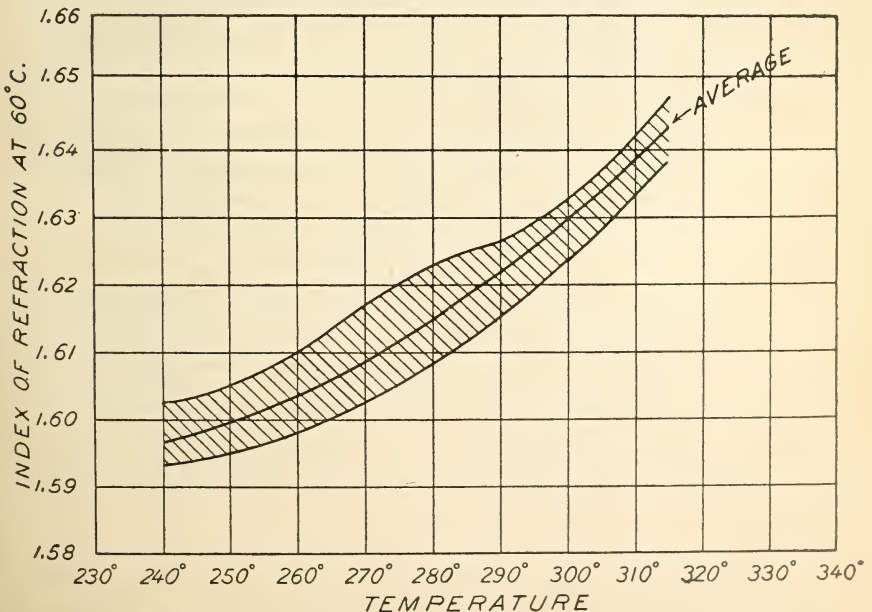


FIG. 8.—Range of indices of refraction of pure coal-tar creosotes.

There are 14 of these oils, and in every case all of the tests which were applied indicated that the oil was obtained from coal alone under the ordinary conditions of rapid high-temperature carbonization. A number of the creosotes were prepared in the laboratory from samples of tar. The numbers and sources of the creosotes used in establishing these limits are given below.

Creosote.	Source.
13-----	Commercial creosote.
15-----	Commercial creosote.
17-----	Distilled from gas-plant tar between 170° and 290°, Westmoreland coal.
18-----	Distilled from gas-plant tar, 170°-315°, Westmoreland coal.
22-----	Distilled from a coke-oven tar, 185°-315°.
25-----	Distilled from a coke-oven tar, 225°-345°.
40-----	Commercial creosote.
42-----	Commercial creosote.
43-----	Commercial creosote.
51-----	Commercial creosote made from a coke-oven tar produced from mixed coals.
62-----	Commercial creosote.
65-----	Distilled from a gas-plant tar, Westmoreland coal.
66-----	Distilled from a gas-plant tar, 200°-360°, Westmoreland coal.
69-----	Distilled from a gas-plant tar, 220°-310°, Westmoreland coal.

#### SPECIFIC GRAVITY.

The specific gravity of the different fractions was determined by the use of small specific-gravity bottles, with a capacity of approximately 10 c. c. Each bottle was numbered and the weight of water which it would contain at 60° was determined. In taking the specific gravity of a fraction, the melted oil was poured into a bottle, which was set in a thermostat and kept at 60° for twenty minutes. The stoppers were then inserted in the bottles, the excess of oil wiped off, and, after cooling, the weight of oil in each bottle determined. Therefore the specific gravities which were determined were equal to

$$\frac{\text{wt. of unit vol. of oil at } 60^{\circ}}{\text{wt. of unit vol. of water at } 60^{\circ}}$$

It very frequently happens that the volume of oil in one fraction is too small for a gravity determination. In such cases it is necessary to unite two or three adjacent fractions and assign the value found to the mean temperature of the fractions used. The specific-gravity curves of creosotes Nos. 40 and 62 are shown in figure 9. The range of specific gravity in which the fractions from the authentic creosotes fall is shown in figure 10.

#### SULPHONATION TEST.

In contradistinction to the hydrocarbons of the paraffin series, those of the aromatic series react with concentrated sulphuric acid with

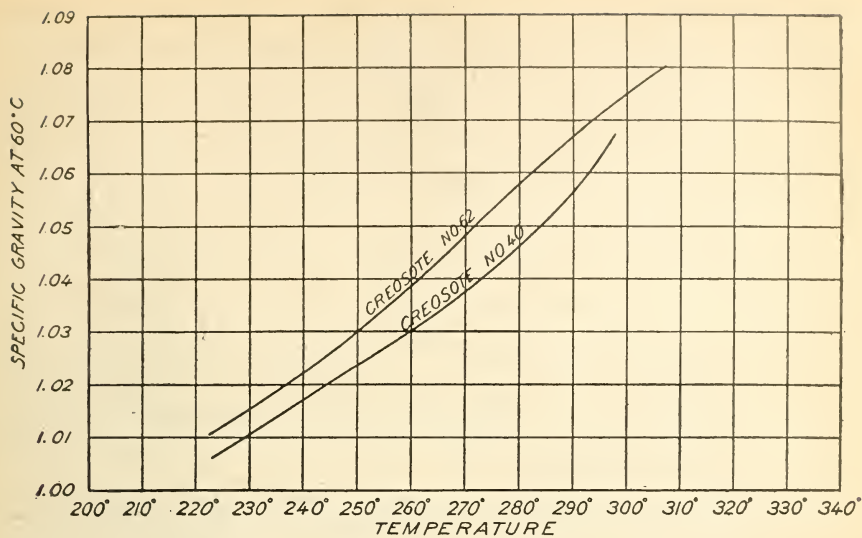


FIG. 9.—Specific gravities of creosotes 40 and 62.

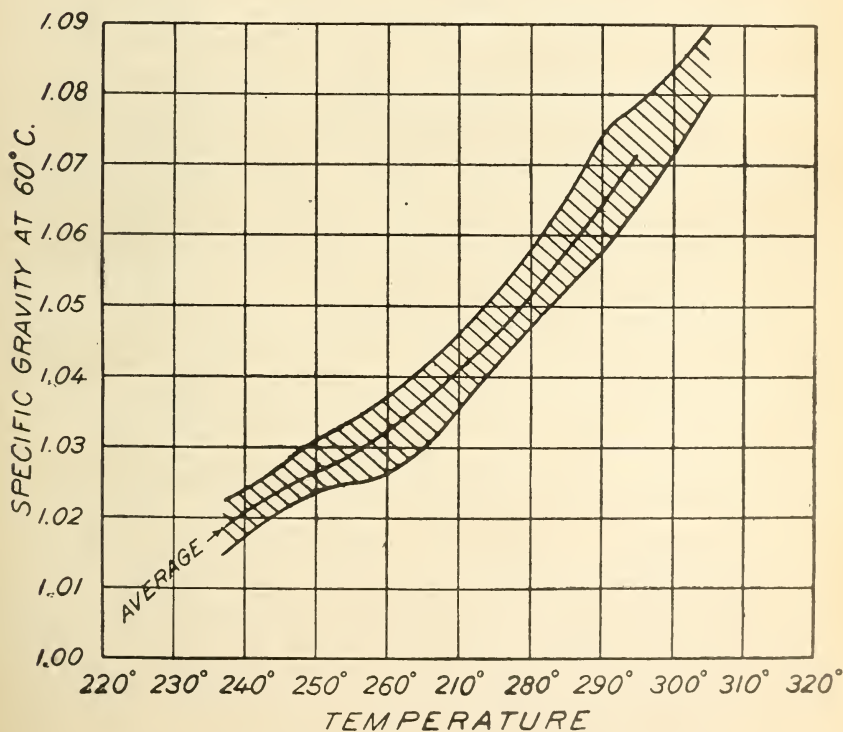


FIG. 10.—Range of specific gravities of pure coal-tar creosotes.

marked ease. The products of this reaction, in which a sulpho group or groups replace hydrogen in the aromatic compound, are called sulphonic acids and the process is known as sulphonation. For example, the reaction with benzene would be  $C_6H_6 + H_2SO_4 = C_6H_5SO_3H + H_2O$ . The sulphonic acids are characterized by their solubility in water. If a fraction from the distillation of a creosote oil be treated under proper conditions with concentrated sulphuric acid, it will be converted into a mixture of sulphonic acids, which will readily dissolve in water. If, however, there are paraffin bodies present they will not be attacked to the same degree as the aromatic hydrocarbons, and when the products of the sulphonation are treated with water the paraffin components will remain as a residual oil. In applying this test to creosote oils it has been found that the most information is obtained by using it on the higher boiling fractions. The first tests were carried out as follows:

The whole of the fraction distilling between  $300^\circ$  and  $320^\circ$  or  $320^\circ$  and  $360^\circ$  was treated in a small flask with four or five volumes of concentrated sulphuric acid. The mixture was heated in the water bath to about  $60^\circ$ , which melted the oil and started the reaction. From this point the reaction proceeded by its own heat; the flask was removed from the water bath and allowed to stand, with intermittent shakings, for thirty minutes. By this time the temperature had fallen, and a further small amount of concentrated acid was added. If the temperature rose again it was an indication that sulphonation was not complete, so that more acid and a longer shaking was required. When the addition of sulphuric acid gave no rise in temperature, the mixture was cooled, diluted with one or two volumes of water, and poured into a 1-liter separatory funnel, with the addition of a large volume of water. The separatory funnel and its contents were allowed to stand for at least an hour to allow the mixture to become clear and any oil to rise as a layer to the surface. After the contents of the funnel had cleared, the aqueous solution was drawn off from the bottom and a fresh portion of water added to any residual oil. In cases of incomplete sulphonation, the oil which was left, when washed with this second portion of water, did not readily float to the surface. Under such circumstances salt was added to increase the specific gravity of the aqueous portion and, after the water was drawn off, the oil was treated with another small portion of concentrated sulphuric acid; the presence of water in the funnel caused a rise in the temperature, so that heating was unnecessary. If the sulphonation is complete any oil residue will be lighter than water. A drop of the residual oil was tested by the refractometer. The index of refraction was always found to be in the petroleum oil



range. None of the oils in the list on page 18 gave any oily residue after sulphonation, which indicates that coal tars produced in coke ovens or gas retorts by rapid high temperature distillation contain no appreciable quantities of paraffin compounds. It sometimes happens that with a true coal-tar creosote a small, oily residue is obtained. Such a residue, however, will be found perfectly soluble in caustic alkalies.

#### PROPERTIES OF OILS OTHER THAN COAL-TAR CREOSOTE.

##### PETROLEUM.

The use of crude petroleum or crude petroleum residues from which some of the constituents have been removed for carburetting gas has led to investigations of the composition of these gas-making oils. Ross and Leather<sup>a</sup> have contributed two very instructive papers on the valuation of gas-making oils. These workers have found that the best test which may be applied to any oil, aside from an actual gas-making experiment, is to make a fractional distillation and determine the index of refraction and specific gravity of the various fractions, particularly of that distilling between 280° and 300°. From a careful study of a number of oils, by actual gas-making tests, by chemical investigations, and by the determination of the two physical properties mentioned, Ross and Leather have found that there is a certain correlation between the index of refraction and specific gravity on the one hand and the character of the hydrocarbons and the gas-making value of the oil on the other. A general conclusion from their work is that oils with low index of refraction and specific gravity are more easily cracked—that is to say, they are more unstable than those with high index of refraction and specific gravity. Moreover, the different groups of hydrocarbons are roughly distinguishable by the determination of these two physical properties. The specific gravity and index of refraction of the distillate from petroleum, between any given temperatures, are very much lower than those from a creosote. This is due to the much lower indices of refraction and specific gravities of paraffin and olefine bodies than of those which have similar boiling points but contain benzene rings.

The index of refraction of the distillates from samples of California petroleum from which the lighter portions had been removed is shown in figure 11, and the specific gravity of the fractions in figure 12. It will be seen that the figures for both specific gravity and index

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<sup>a</sup> The Constitution of Gas Oils, Journal Society of Chemical Industry, 21: 676.

Composition and Valuation of Oils Used for Gas Making Purposes. Analyst, 31: 284.

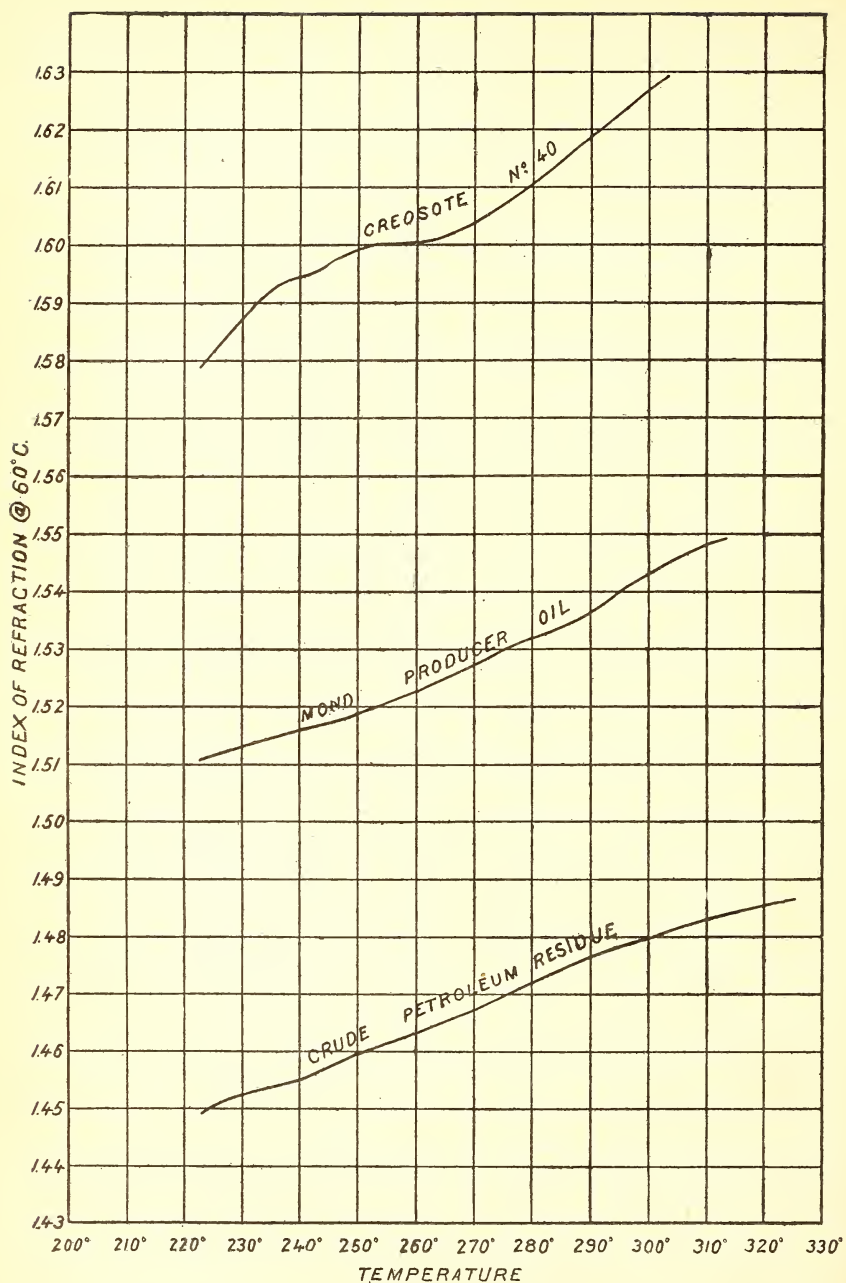


FIG. 11.—Indices of refraction of creosote 40, Mond producer oil, and crude petroleum residue.

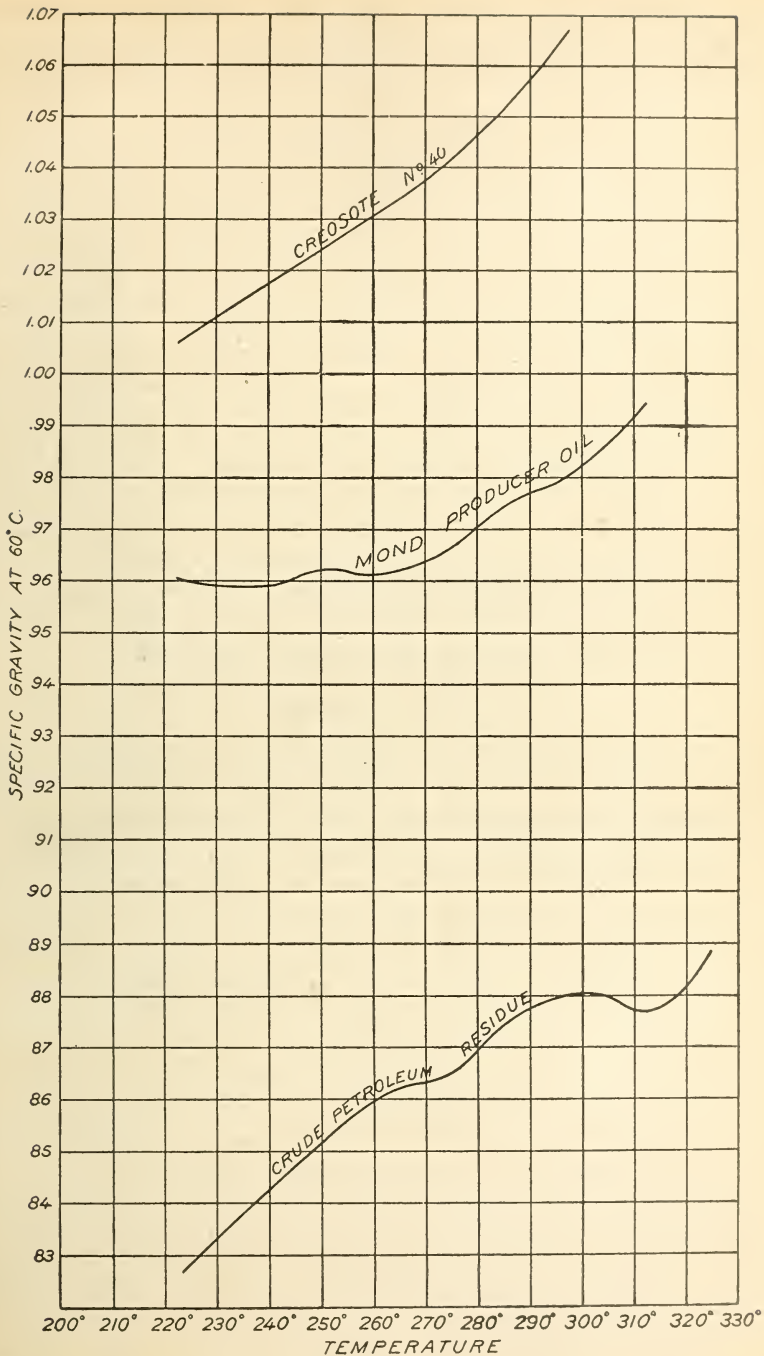


FIG. 12.—Specific gravities of creosote 40, Mond producer oil, and crude petroleum residue.

of refraction are very much lower than the corresponding values for creosote. Crude petroleum also gives a very large sulphonation residue.

#### OIL FROM MOND PRODUCER TAR.

There are a number of forms of gas producers in which bituminous coal is used instead of oil. In these producers the coal is burned with the admixture of air and steam. Tar is formed as a by-product, and on distillation it yields an oil with a distillation range similar to that of creosote. The odor of a bituminous producer oil is easily distinguished from that of either creosote or petroleum. A sample of oil obtained from the tar made in a Mond producer, one type of a gas-making machine using bituminous coal, has been examined in the Forest Service laboratory. The oil in question was dark colored and free from a naphthalene sediment. The indices of refraction and the specific gravities of the different fractions distilled from this oil are shown in figures 11 and 12. The producer oil is characterized not only by its low index of refraction and specific gravity, but by the very high content of alkali-soluble bodies. The "tar acids" in the portion distilling up to 250° were 47 per cent by volume; from 250° to 300°, 35 per cent; and from 300° to 340°, 30 per cent.

#### OIL-GAS TAR CREOSOTE.

A very large amount of tar is manufactured in the United States in gas producers, in which petroleum oils are cracked at very high temperatures. The greater part of this oil gas is made in connection with water-gas production. The water gas, composed of gases which burn with a nonluminous flame, must be enriched for illuminating purposes, and it is in these water-gas carburetors that the greater part of the oil tar is produced. This tar is finding various uses. Some of it is used for fuel, and not inconsiderable quantities are distilled for pitch. In distilling oil-gas tars a fraction is obtained with the same boiling-point range as that from coal tar. The odor of this creosote from oil tar is sometimes very distinctive; in other cases it is less pronounced. Fractional distillations show that these creosotes approach much more nearly the products of coal-tar distillations than either crude petroleum or the bituminous producer oils. In fact, the resemblance between fractions from a true coal-tar creosote and an oil-tar creosote is striking. In both cases the low-boiling liquid fractions are followed by solid naphthalene distillates, then by a liquid portion, and finally at the high temperatures by a yellow solid distillate.

Creosotes have been prepared at the Forest Service laboratory from a number of oil tars made in various parts of the country. These



tars differ considerably in general character; some are very much thinner than others. The creosotes obtained from them likewise show considerable variation, particularly in the amount of naphthalene which settles out of them on cooling. The distillation curves from two typical oil-tar creosotes are shown in figure 13.

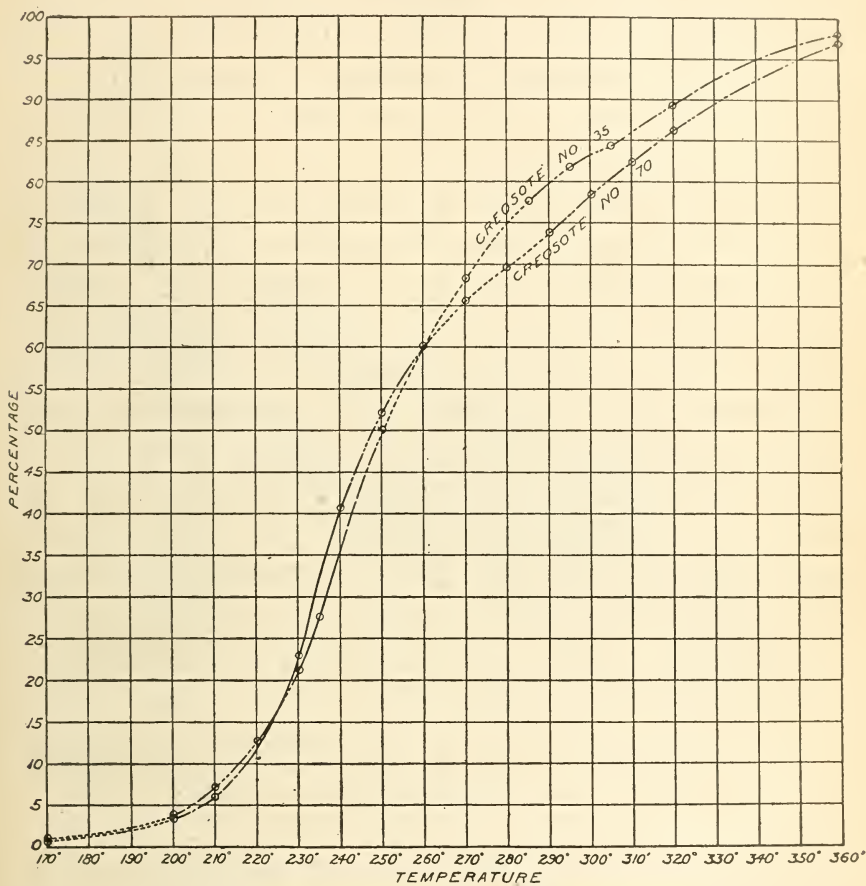


FIG. 13.—Distillations of two typical oil-tar creosotes.

The differences in odor, color, and other general characteristics of the distillates from pure coal-tar creosote and oil-tar creosote are sufficient to enable one experienced in creosote analysis to distinguish readily between the two. In no case have fractions distilling from coal-tar creosote above 320° been found to melt as low as 60°, whereas it is the rule for similar fractions from oil-tar creosotes to melt at that temperature. In distilling one oil-tar creosote of high boiling range, fractions were obtained above 360° which were liquid, but be-

came gelatinous on standing.<sup>a</sup> The indices of refraction and the specific gravities of the various fractions distilling from a number of oil-tar creosotes have been determined and the results are plotted in figures 14 and 15.

It will be seen from these data that both the specific gravity and the index of refraction is lower in the case of the oil-tar creosotes than in that of the coal-tar creosotes. Moreover, the high boiling fractions of the oil-tar creosotes always yield an oily residue from the sulphonation test. The index of refraction of this residuum is very low, falling in the general range of crude petroleum. This in-

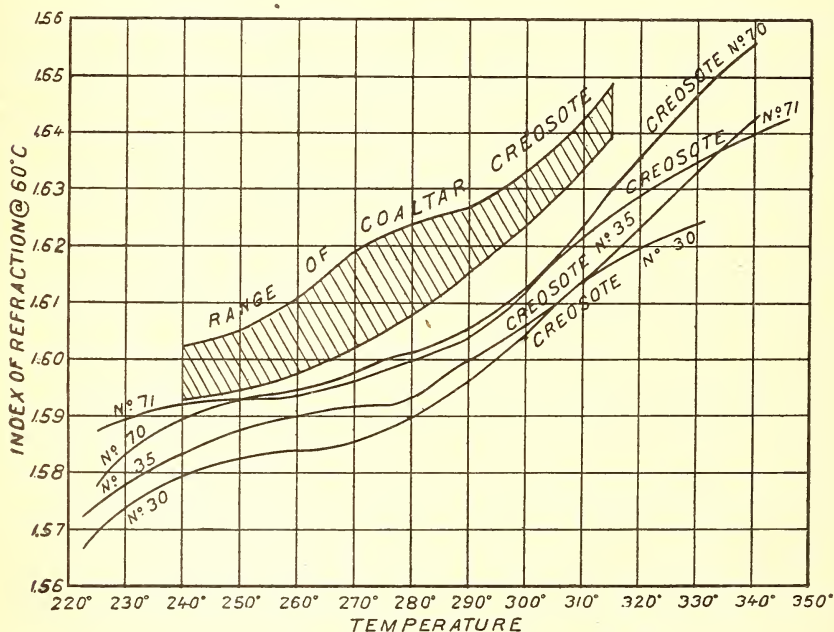


FIG. 14.—Indices of refraction of oil-tar creosotes.

icates that some of the gas-making oils get through the producer without being decomposed, and appear in the tar. It is, of course, the object of the gas engineer to prevent this as far as possible, and to obtain from his oil the highest possible yield of gas.

#### PROPERTIES OF MIXTURES OF COAL-TAR CREOSOTE AND OTHER OILS.

Although it is not difficult to distinguish between coal-tar creosote and the oils which are offered as substitutes for preserving timber, the detection of these other oils in admixture with true creosote is a

<sup>a</sup> Later work upon oil-tar creosotes show this to be a characteristic property.

matter of some difficulty. If the admixture of foreign oils is large the odor may excite suspicion. If the fractions distilling above  $320^{\circ}$  will melt under  $60^{\circ}$  it is an indication that a more thorough examination of the creosote is needed.

On account of the great difference between the physical constants of creosote and of crude petroleum, relatively small quantities of petroleum are readily detected by determining the specific gravities and indices of refraction of the high-boiling fractions distilling from the mixture. An admixture of 10 per cent of petroleum to a creosote like

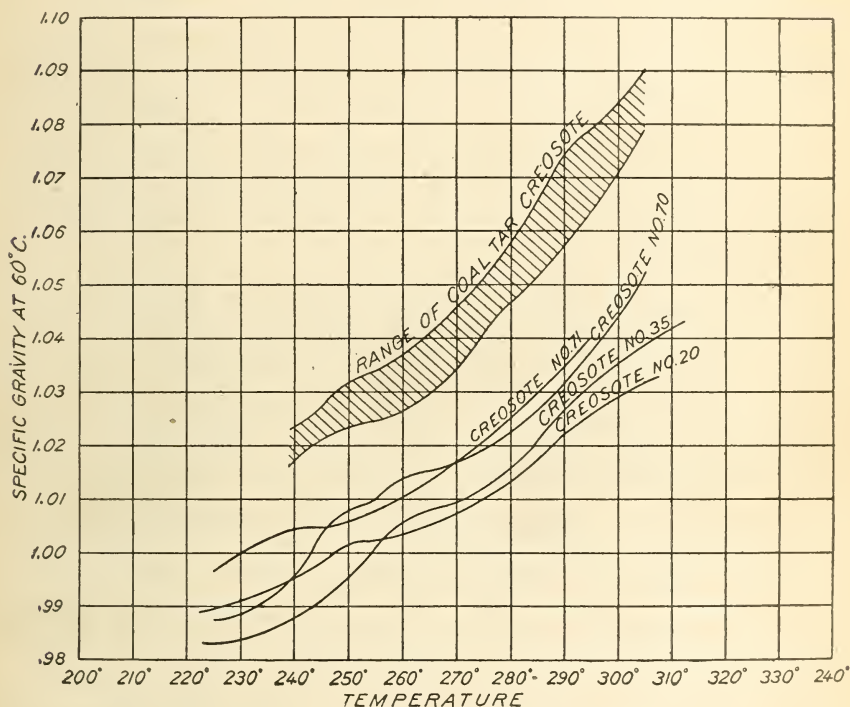


FIG. 15.—Specific gravities of oil-tar creosotes.

No. 40, which is of the lower-boiling type, will throw the index of refraction out of the range of pure coal-tar creosotes as given in figure 8, and a sulphonation residue with a low index of refraction will be obtained from the high-boiling fractions. If the same amount of petroleum were added to a high-boiling oil, the index of refraction, although noticeably lowered, would not fall outside of the creosote range; but a sulphonation residue would be obtainable. Along with the lowering of the index of refraction, the specific gravity of the fractions will also drop.

The addition of a bituminous producer oil will affect the physical constants in the same general way as crude petroleum, but there will be no sulphonation residue.

On account of the much higher values of the physical constants of the distillate from oil-gas tar as compared with those of the constants of petroleum or bituminous producer oil, the properties of the creosote are not as seriously affected by the addition of small quantities of the oil-tar creosote as by the admixture of one of the others. The addition of less than 25 per cent of oil-tar creosote to a coal-tar creosote will usually not affect its index of refraction and specific gravity sufficiently to give an infallible proof of the adulteration, unless the coal-tar creosote used in the mixture is a very low boiling one. Small quantities of oil-tar distillates may make their presence known by the results of the sulphonation reaction. Some of the creosotes on the market show such low curves of index of refraction and specific gravity and such large sulphonation residues as to indicate a generous use of oil-gas tar somewhere in the process of their production.

In the Forest Service investigations only one creosote of undoubted purity has been found which gave values similar to those of the mixtures of oil-tar and coal-tar creosotes. This one oil was made in the laboratory from a tar of unquestionable authenticity. In the production of this tar, however, a not inconsiderable portion of the coal in each charge was incompletely carbonized and must have been distilled at relatively low temperatures. Since such treatment of coal gives a tar containing paraffin compounds, it is not surprising that this creosote should show a range of properties comparable to mixtures of coal-tar and oil-tar creosotes. It is only because of the very rare occurrence of such low temperature distillations of coal that the properties which have been worked out for true coal-tar creosotes can be depended upon.

Some adulterated creosotes have come into the Forest Service laboratory the exact nature of the adulteration of which was not known. These particular oils differed in their viscosity from coal-tar creosote to a marked degree. The viscosities of different samples of pure coal-tar creosotes show very little variation; the heavier, high-boiling oils are only slightly more viscous. If the viscometer is standardized with water at 60°, and then the number of seconds required for the same volume of any oil at 60° to pass through the viscometer is noted, the specific viscosity of the oil is found by dividing the number of seconds required for the oil by the number of seconds required for water. This specific viscosity rises with the specific gravity, and the ratio between specific viscosity and specific gravity is very nearly



constant for pure coal-tar creosotes. The peculiarly adulterated oils mentioned above, when tested by this procedure, were found to have markedly higher viscosities. It is not known whether this increased viscosity would hinder the penetration of wood by these oils.

#### VALUE OF THOROUGH CREOSOTE ANALYSES.

The efforts to develop the analysis of creosote in this country have been largely directed to securing uniformity of procedure. Uniformity of creosote analysis is absolutely necessary in the trade, but the results which have been detailed indicate that something else than uniformity is desirable. Volatility tests and the analyses of creosote used in open-tank treatments prove that different oils have very different values for these treatments. The water in creosote and the oils which distill under  $210^{\circ}$  are practically all waste. The difference in loss between two oils, one with 15 per cent of distillate under  $210^{\circ}$  and the other with only 2 per cent, is so great that it would be economy in an open-tank method to use a smaller quantity of a high-boiling oil, despite the somewhat greater original price, than a larger quantity of a low-boiling oil. In the case of the oils used in the open-tank experiments shown in figure 1, where there was a loss of 40 per cent, if the actual price of the creosote, including freight charges, drayage, etc., had been 10 cents per gallon, the cost of the oil finally placed in the timber would have been  $16\frac{2}{3}$  cents. In small lots the difference may not be great enough to warrant a thorough analysis, but where quantities like 100,000 gallons are being purchased losses of this sort amount to very substantial figures.

The increasing tendency toward sophistication of creosotes also makes it necessary to be watchful in buying. It is not a question of whether the distillates from other tars are as valuable or nearly as valuable as coal-tar creosote, since it is obvious that the purchaser should receive for use the article for which he is paying, and if he is to use distillates from other tars he should do so with his eyes open, reserving for himself the privilege of deciding what is best.

#### A NEW METHOD OF DISTILLING CREOSOTE.

In view of the value of thorough creosote analysis, it is worth while to attempt to perfect the method of distillation used in these analyses. From the results which were detailed in Circular 80, it is evident that the ordinary distilling flask is not an efficient apparatus for the lower-boiling portions of creosote, and is, in fact, little better than the retort. To attempt a redistillation of the fractions is tedious and time consuming. In endeavoring to use an efficient still head the tendency

of some portions of the creosote distillate to solidify prevents the use of such an apparatus as the Lebel-Henninger distillation tube. A Hempel column seems to be the best adapted for fractioning creosotes, since it prevents solidification and is easily cleaned.

A special distilling flask, in which the Hempel column is placed between the bulb and outlet tube, was designed for this purpose and is shown in figure 16. The constricted portion of the neck serves to hold up a loose plug of coarse platinum wire, which supports the glass beads above. The flask, shown in the figure, holds 200 large beads, leaving ample room for the bulb of the thermometer above the beads

and below the outlet tube. Using this distilling bulb and 250 grams of oil, a separation is effected, which experiment shows to be better than a redistillation, as shown by the curves in figure 17.

The light oil is separated from the naphthalene very much more effectively than by the ordinary distilling flask, and the naphthalene fractions from most oils are so rich in naphthalene that they will not melt at 60°. It will be seen that the difference in efficiency is most evident in the low-boiling fractions, the fractions which distinguish most accurately the variations in value between different oils. In these distillations the bulb was supported on an asbestos board, in which a hole was cut almost as wide as the largest diameter of the

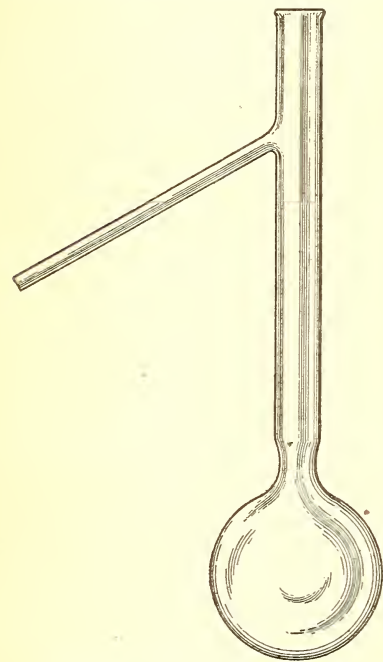


FIG. 16.—Hempel distilling flask.

bulb. The outline of this opening was not regular, but notched to allow small portions of the flame to play up around the bulb. The portion of the distilling bulb above the asbestos board and below the Hempel column was surrounded by an asbestos box. The source of heat was an Erlenmeyer-Argand burner. With this arrangement a moderate amount of heat was sufficient to give an excellent distillation through the Hempel column. The distillations were run at the rate of a drop per second. The thermometer was placed with 200° the first emergent reading, and observations showed that the value  $t$  was almost exactly the same as with the ordinary 500 c. c. flask. After a distillation the beads and platinum plug were removed before

complete cooling caused them to become too sticky. The platinum plug was held in the flame until clear, and the beads were allowed to collect in a wide-mouth bottle of alcohol until a sufficient quantity was collected for a wash-up.

Not only do the percentage weight curves show that this new distilling bulb is giving a much better fractionation, but the in-

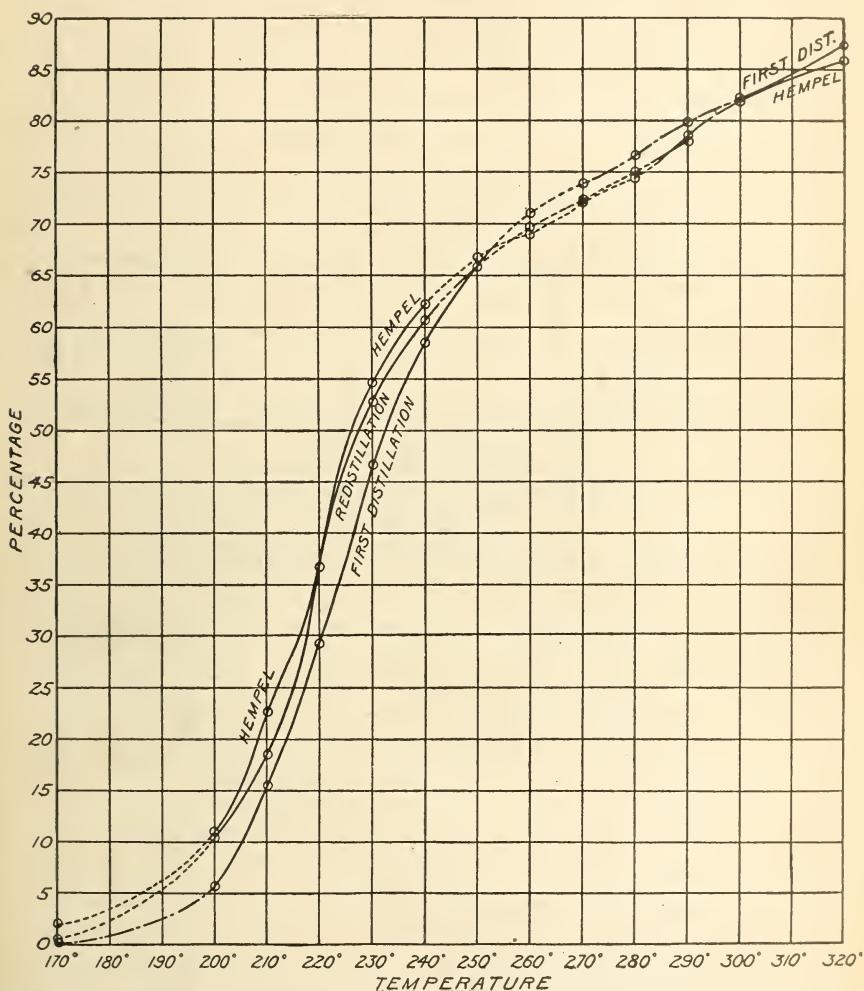


FIG. 17.—Comparison between distillation with Hempel flask and redistillation with common flask.

indices of refraction and the specific gravities of the fractions show a much sharper separation of the constituents of the creosote. These facts are illustrated in figures 18 and 19.

The shape of the range curve into which the indices of refraction of the portions of pure coal-tar creosote fall is altered somewhat

by the use of the new distilling bulb, and the differences between pure coal-tar creosote and other oils are brought out more graphic-

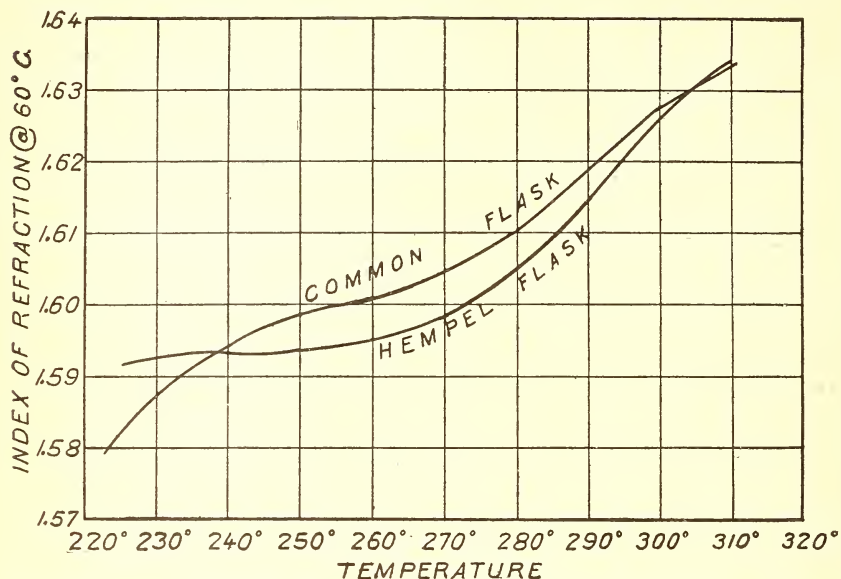


FIG. 18.—Comparison between indices of refraction of distillations with Hempel flask and with common flask.

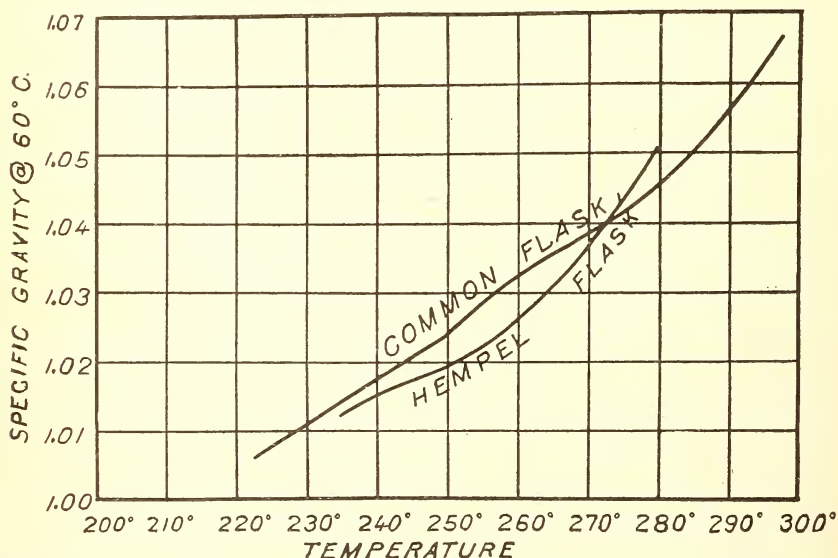


FIG. 19.—Comparison between specific gravities of distillations with Hempel flask and with common flask.

ally. The range of indices of refraction with the new bulb is shown in figure 20.

[Cir. 112]



Too few determinations of the specific gravities of pure creosotes have been made to furnish data for a range, but the values for the creosote which gave the lowest results when distilled from a common flask are shown in figure 21.

### CONCLUSIONS.

From the experience of the Forest Service in the analysis of oils, the results of a portion of which have been detailed above and in Circular 80, it seems desirable that there should be two methods of analyzing creosote. One, which may be called a field method, very similar to the present method of the Wood Preservers' Asso-

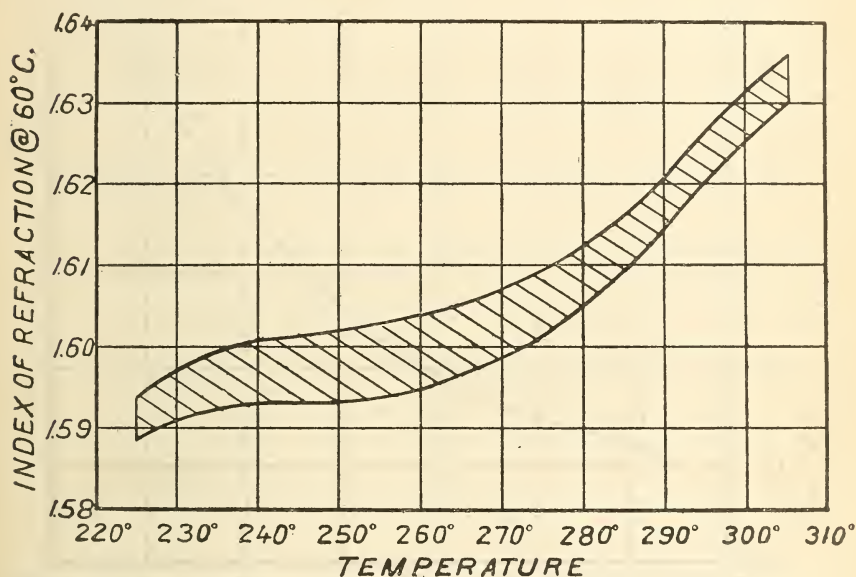


FIG. 20.—Range of indices of refraction of pure coal-tar creosotes distilled from Hempel bulb.

ciation, is to show the general character of the oil under analysis; the other, which may be called a laboratory method, is adapted to the analysis of an oil which for any reason requires careful examination. This latter more exact method would be useful in analyzing oils to be used in the experimental treatments conducted by the Forest Service and in commercial work where a large amount of creosote is being purchased, or where the delivery of an oil not up to specifications is suspected.

### FIELD METHOD OF ANALYSIS.

The field method of analysis includes two determinations—the specific gravity of the oil and a fractional distillation.

## SPECIFIC GRAVITY.

The perfectly liquefied oil is poured into a hydrometer cylinder, and, at a temperature of 60°, the specific gravity is read with a hydrometer standardized against water at 60°.

The somewhat prevalent method of determining specific gravity with a hydrometer standardized at 15° and then calculating the results from the temperature of the determination back to 15° is round-about and involves the expression of the specific gravity of creosote in the liquid condition at a temperature at which the oil does not

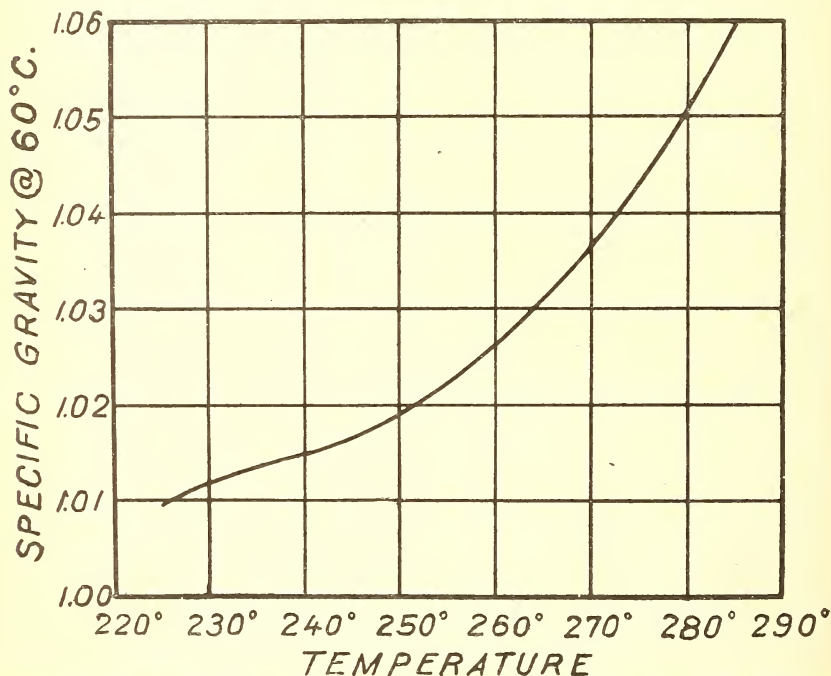


FIG. 21.—Lowest specific gravity obtained for a pure coal-tar creosote distilled from Hempel bulb.

exist as a liquid. The method is illogical and open to inaccuracies. With very rare exceptions creosotes are all liquid at 60°, and if the weight of a unit volume of the oil at 60° is compared with the weight of a unit volume of water at 60°, a true specific gravity is obtained.

## FRACTIONAL DISTILLATION.

Fractional distillation is conducted in a 200 c. c. distilling flask, the outlet tube of which is placed at approximately half the distance from the base of the neck to the top. The neck is of such a length that when the thermometer is placed with the top of the mercury bulb just below the outlet tube, the first reading on the emergent

stem will be 200°. For the large carbon-dioxide filled thermometers which have been used in the Forest Service laboratory, this means that the distance from the outlet tube to the top of the neck shall be 3 inches. A condensing tube is employed. One hundred cubic centimeters of perfectly liquefied, well-shaken oil is measured at 60° into the distilling flask with a pipette. The distillation is conducted not faster than 2 drops per second nor slower than 1 drop per second, and the following fractions are collected:

1. Up to 205° in a 25 c. c. cylinder.
2. 205° to 235° in a 50 c. c. cylinder.
3. 235° to 250° in a 50 c. c. cylinder.
4. 250° to 295° in a 50 c. c. cylinder.
5. 295° to 320° in a 50 c. c. cylinder.
6. Above 320° in a 25 c. c. cylinder.

At the end of the distillation the four cylinders are set in water kept at between 60° and 65° until the solid fractions are completely liquid. The volume of each fraction is then read and recorded and the difference between the sum of the various volumes and 100 is given as "Residue and loss."

The reasons for using a distillation flask instead of a retort are (1) a slightly better fractionation is obtained; (2) the thermometer correction for the emergent stem is less than for the retort and is uniform with the other distillation method. The measurements are all by volume instead of by weight, because this obviates the necessity of using a balance. The results are not quite as accurate, but the differences are small. For example, distillations of creosotes Nos. 13 and 15, representing heavy and light oils, were made by weight; the results were then calculated into volumes by the use of the specific gravities which had been determined in the detailed distillations conducted in the Service laboratory. The differences are shown in Table 5.

TABLE 5.—*Comparison of percentages by weight and by volume in creosote distillations.*

CREOSOTE NO. 13.

Temperatures.	Grams.	Cubic centimeters.	Per cent by weight.	Per cent by volume.	Difference.
210-250	33.37	33.02	33.37	33.46	+.09
250-270	10.11	9.88	10.11	10.34	+.23
270-300	11.04	10.48	11.04	10.95	-.09

CREOSOTE NO. 15.

170-200	5.84	5.94	5.84	6.10	+.26
200-210	11.36	11.37	11.36	11.57	+.21
210-250	55.23	54.50	55.23	55.10	-.12
250-270	8.27	8.00	8.27	8.20	-.07
270-295	4.99	4.74	4.99	4.87	-.12

It will be noticed that the largest variations obtained in any case were in the lowest fraction of No. 15, in which a difference of about 0.25 per cent is shown. This difference is far within the limits of error in the method of distillation.

An experiment with another oil was carried out as follows: One hundred cubic centimeters of oil at 60° were carefully measured into a tared distilling bulb and the weight taken. Tared graduated cylinders were used for receivers. At the end of the distillation the cylinders were weighed and the weight of each fraction calculated; they were then placed in water heated to 60°, allowed to stand until they had reached that temperature, and the volumes read as percentages. The results are given in Table 6.

TABLE 6—Comparison of percentages by weight and by volume.

Tempera- tures.	Per cent by weight.	Per cent by volume.	Difference.
205	7.9	7.4	-0.5
205-250	32.8	34.0	+1.2
250-300	28.3	28.4	+ .1
300-360	23.8	22.6	-1.2

Here again, the largest variation, 1.2 per cent, is too small to vitiate the results in such a method of analysis. In view of the comparative accuracy of the results the simplicity of the volumetric method makes it the best for the rough analysis of creosotes.

#### LABORATORY METHOD OF ANALYSIS.

Laboratory methods of analysis include (1) determination of the specific gravity of the oil; (2) fractional distillation with the Hempel distilling flask; (3) determination of the indices of refraction of the different fractions; (4) determination of the specific gravities of the different fractions; (5) sulphonation test; (6) determination of phenols or tar acids in the whole oil, and (7) determination of water.

Only rarely will it be necessary or desirable to perform all these processes. Under ordinary circumstances a fractional distillation with the determination of the indices of refraction of the fractions will be sufficient. If the index of refraction or the character of the distillates indicates adulteration of the oil the sulphonation reaction and the specific gravity determinations are desirable. The procedure for the various tests is as follows:

#### SPECIFIC GRAVITY OF THE WHOLE OIL.

This determination is made precisely as in the field method.



## FRACTIONAL DISTILLATION.

The Hempel distilling flask of resistance glass, shown in figure 16, is employed. The empty flask is tared, 250 grams of melted, well-shaken oil introduced, the platinum-wire plug and the glass beads put in place, and a second weight taken. The thermometer is then inserted in the flask, so that the first emergent reading is  $200^{\circ}$ . The flask is supported on an asbestos board with a slightly irregular opening of very nearly the largest diameter of the flask. A condensing tube is employed and the fractions are collected in tared flasks. The distillation is run at the rate of 1 drop per second, and fractions collected between the following temperatures: Up to  $170^{\circ}$ ,  $170^{\circ}$ – $205^{\circ}$ ,  $205^{\circ}$ – $225^{\circ}$ ,  $225^{\circ}$ – $235^{\circ}$ ,  $235^{\circ}$ – $245^{\circ}$ ,  $245^{\circ}$ – $255^{\circ}$ ,  $255^{\circ}$ – $285^{\circ}$ ,  $285^{\circ}$ – $295^{\circ}$ ,  $295^{\circ}$ – $305^{\circ}$ ,  $305^{\circ}$ – $320^{\circ}$ , and, if feasible,  $320^{\circ}$ – $360^{\circ}$ .

The character of the fractions and their weights are recorded and the results plotted as a curve, in which the ordinates are percentages by weight and the abscissæ temperatures. The character of the fractions is indicated by the character of the line—dots representing liquids, solid lines solids, dashes nearly solid consistencies, and dashes and dots the intermediate characters. When the distillation has reached the  $225^{\circ}$  point, an asbestos-board box should be placed around the distilling flask, to cover the bulb, but leave the Hempel column exposed. Drafts upon the distilling apparatus must be avoided.

## INDEX OF REFRACTION.

The indices of refraction of the different fractions between  $235^{\circ}$  and  $305^{\circ}$  are determined at  $60^{\circ}$  in a refractometer with light compensation. The results are plotted with temperatures as abscissæ and indices of refraction as ordinates.

## SPECIFIC GRAVITY.

The specific gravities of the fractions between  $235^{\circ}$  and  $305^{\circ}$  are determined by means of specific gravity bottles. These bottles are filled at  $60^{\circ}$  and the weights referred to water at the same tempera-

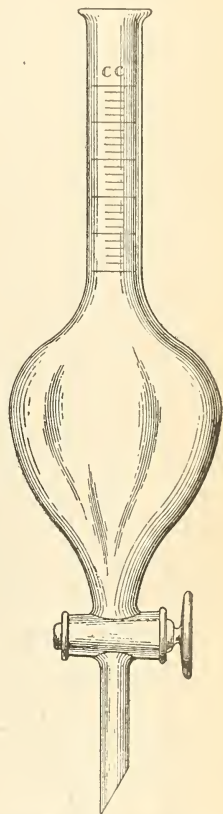


FIG. 22. — Separatory funnel for sulphonation test.

ture. The results are plotted as a curve, in which the ordinates are specific gravities at 60° and the abscissae temperatures.

#### SULPHONATION TEST.

The fraction distilling between 305° and 320° is treated with concentrated sulphuric acid and poured into a special separatory funnel,

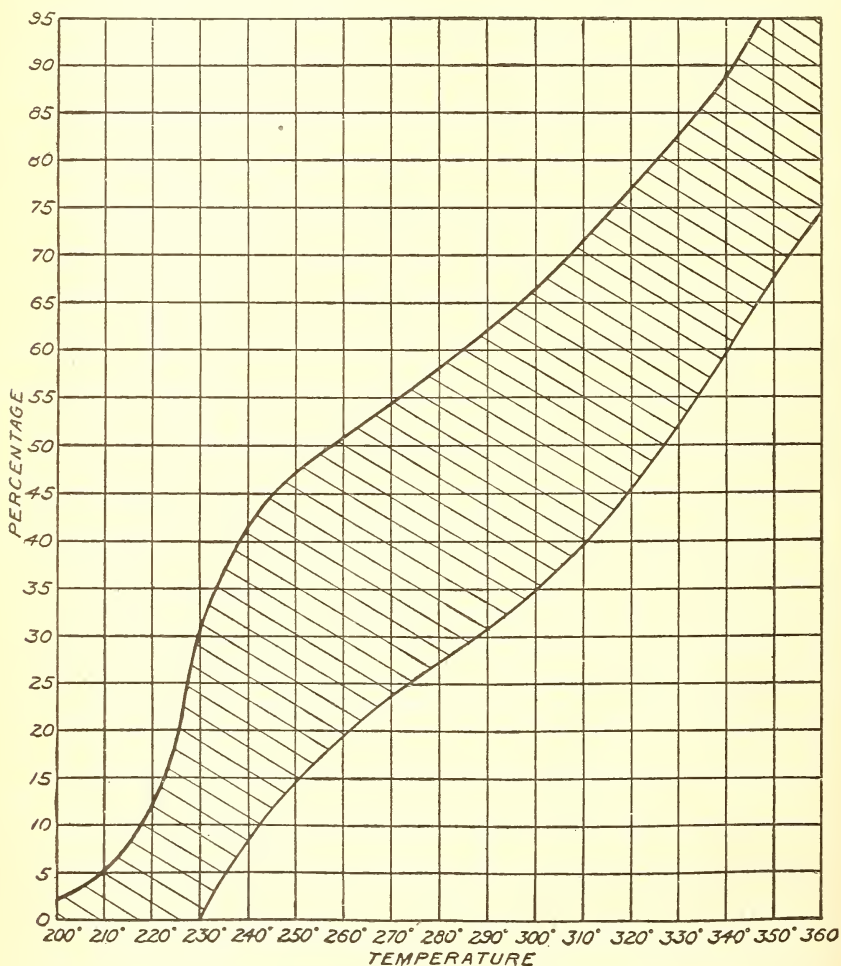


FIG. 23.—Distillation limits for Grade A.

such as is shown in figure 22. The flask which contained the fraction is rinsed out twice more with concentrated sulphuric acid and the rinsings added to the funnel. Enough more concentrated sulphuric acid is added nearly to fill the funnel, and the mixture is thoroughly shaken at least six times in thirty minutes. After standing

until it becomes cool the volume is brought up into the graduations by the addition of concentrated sulphuric acid, and after another hour the amount of unsulphonated oil is read and the percentage calculated. The residual oil is usually almost white or a pale blue. In some cases a reddish oil with a distinctive odor is obtained from a

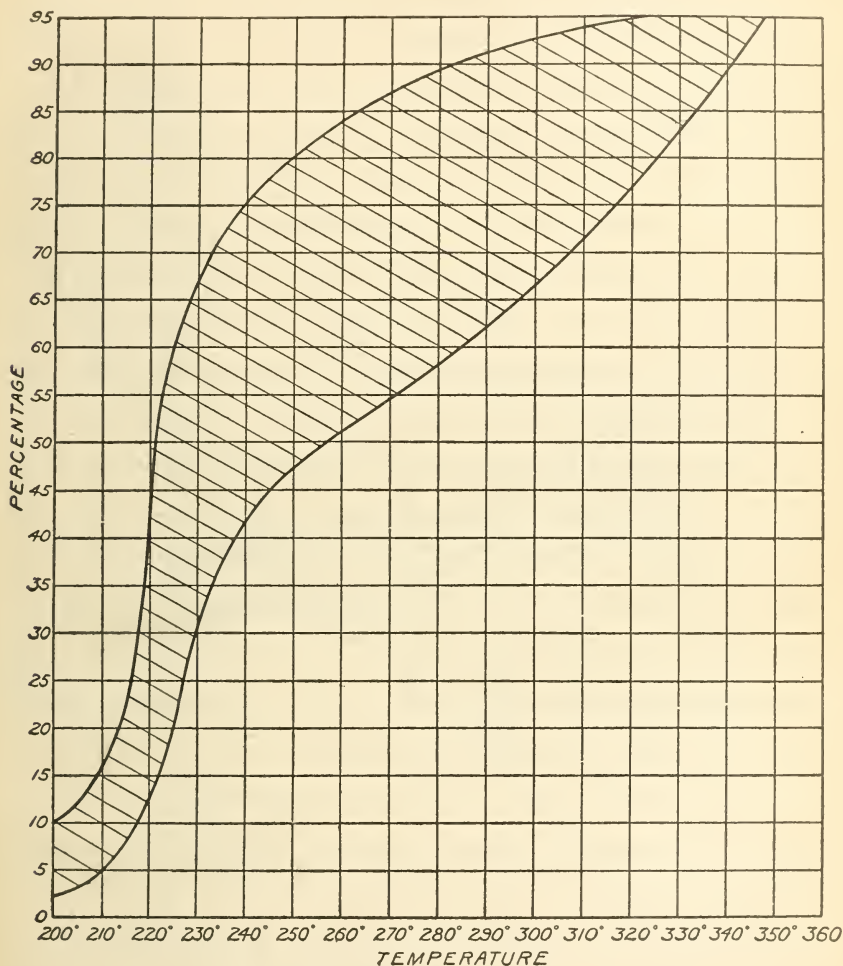


FIG. 24.—Distillation limits for Grade B.

pure coal-tar creosote; this oil does not consist of hydrocarbons and is soluble in caustic alkalies. The sulphuric acid should, therefore, be drawn off, the oil washed with water, and a 10 per cent solution of sodium hydroxide added. If the oil is soluble in this reagent, the sulphonation test is regarded as negative.

Fifty cubic centimeters of the creosote under analysis are measured at 60° into a small distilling flask by a pipette. The oil is distilled as completely as possible without breaking the distilling bulb, and the

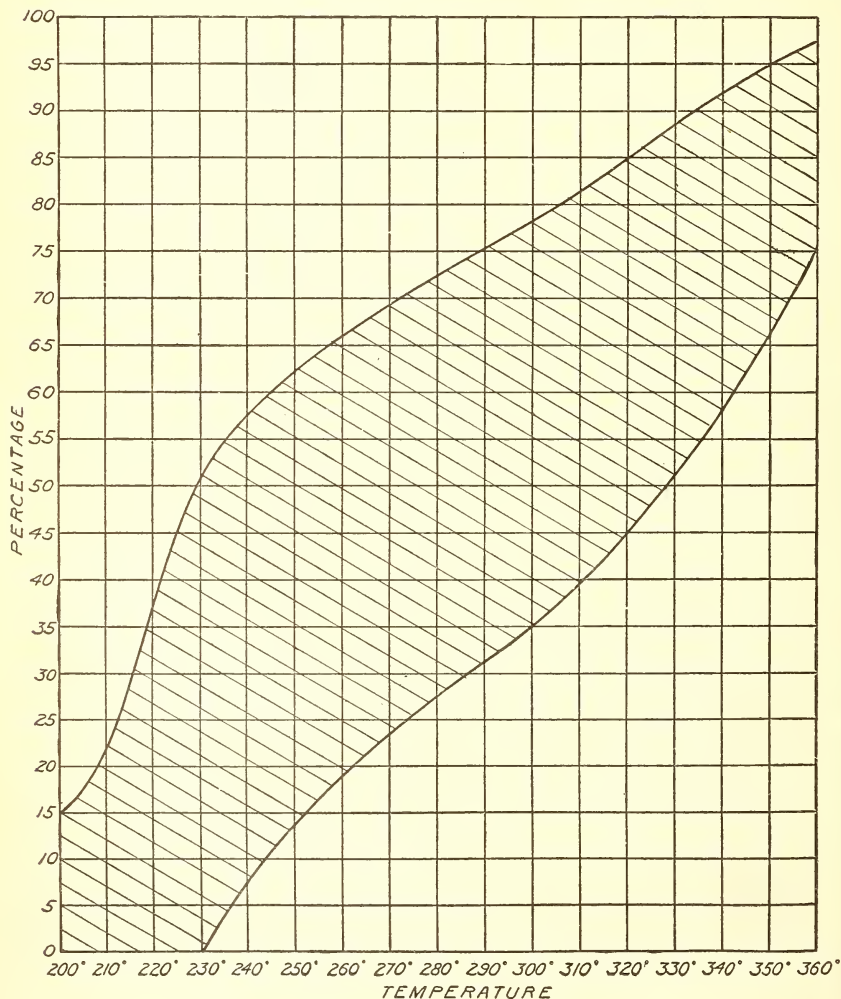


FIG. 25.—Distillation limits for Grade C.

distillate is caught in a short-stemmed, 100 c. c. separating funnel. At the end of the distillation 25 c. c. of boiling hot 15 per cent sodium hydroxide is added to the distillate and the mixture thoroughly shaken. The alkaline extract is then drawn off into a 100 c. c. shaking cylinder and 25 c. c. more of hot sodium hydrox-



ide added. After extracting with this second portion for five minutes, with frequent shaking, the solutions are allowed to separate and the alkaline extract added to the first portion in the cylinder. A third extraction is made with 15 c. c. of alkali. The total alkaline extract is cooled, acidified with sulphuric acid, thoroughly shaken, brought to 60°, and the volume of supernatant oil read off.

#### WATER.

After weighing the first two fractions of a fractional distillation they are united in a small separatory funnel and any water which is present is separated from the oil and its amount accurately de-

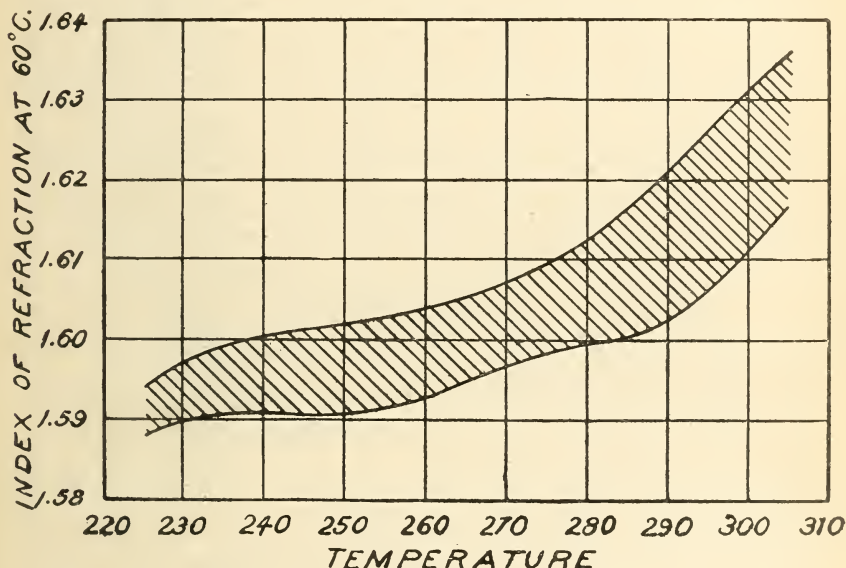


FIG. 26.—Index of refraction limits for Grade C.

terminated. If particular accuracy is required in the estimation of the water it may be done by the Marcusson xylol distillation method.<sup>a</sup>

#### GRADES OF CREOSOTE.

The various methods of creosoting timber and the various purposes for which creosoted timber is intended indicate so strongly the varying values of different sorts of oil that the following four grades are tentatively proposed:

*Grade A.*—On a fractional distillation, according to the laboratory method outlined above, the distillation curve shall fall within the

<sup>a</sup> Forest Service Circular 134, "The Estimation of Moisture in Creosoted Wood."



shaded limits shown in figure 23. The indices of refraction at 60° of the fractions shall not fall more than 1 in the third place of decimals below the range in figure 20, and the specific gravities at 60° shall not fall more than 1 in the third place of decimals below the lower limit shown in figure 21. On applying the sulphonation test to

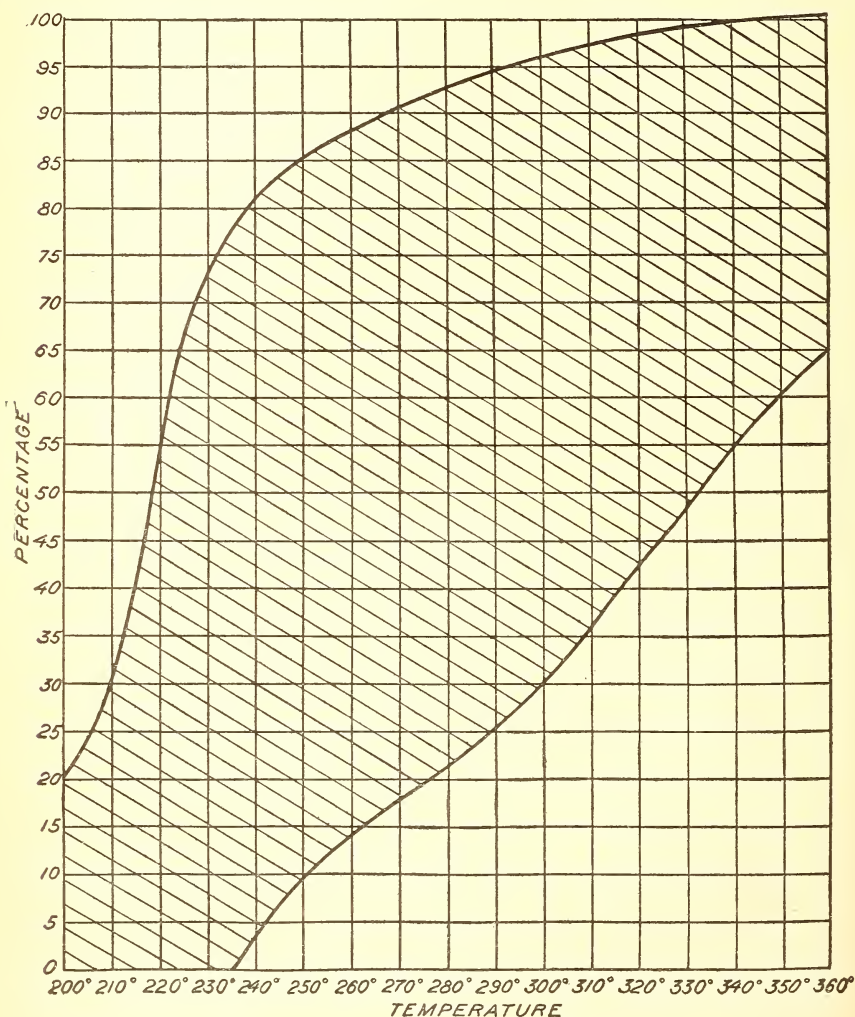


FIG. 27.—Distillation limits for Grade D.

the fraction between 305° and 320° there shall be no oily residue insoluble in caustic alkalis. The water shall not exceed 1 per cent. There shall be no admixture of undistilled tar.

*Grade B.*—The percentage weights on distillation by the laboratory method shall fall within the shaded limits in figure 24. The

specifications for index of refraction, specific gravity, and sulphonation test are the same as for Grade A. The water shall not exceed 2 per cent. There shall be no admixture of undistilled tar.

*Grade C.*—The percentage weights on distillation, according to the laboratory method, shall fall within the limits shown in figure 25, and the indices of refraction shall fall within the limits shown in figure 26. The volume of the sulphonation residue in the fraction,  $305^{\circ}$ – $320^{\circ}$ , shall not be greater than one-tenth of the weight of the fraction. The water shall not exceed 4 per cent. There shall be no admixture of undistilled tar.

*Grade D.*—The distillation limits are shown in figure 27, and the

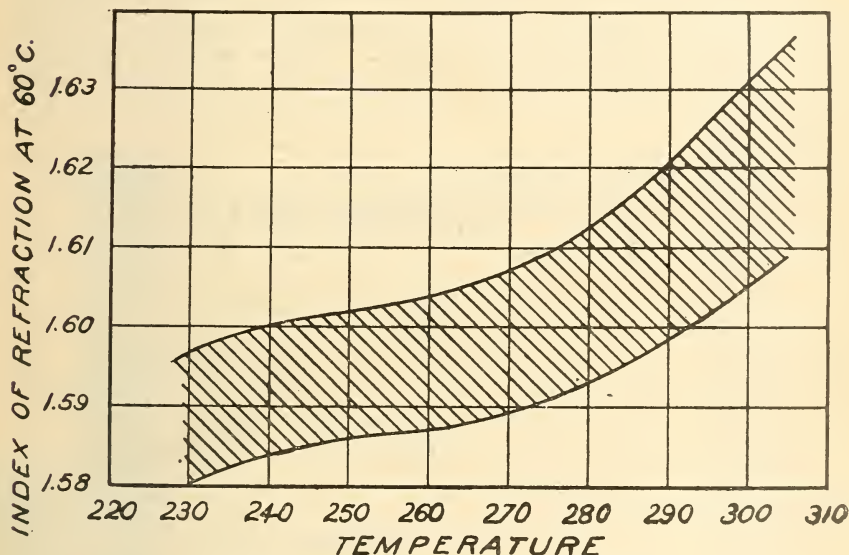


FIG. 28.—Index of refraction limits for Grade D.

indices of refraction shall fall within the limits shown in figure 28. The volume of the sulphonation residue from the fraction,  $305^{\circ}$  to  $320^{\circ}$ , shall not exceed one-fifth of the weight of that fraction. The water in the creosote shall not exceed 5 per cent, and admixture of undistilled tar or other viscous material shall not exceed 15 per cent.

#### USES OF THE VARIOUS GRADES.

The Grade A oil is adapted for open-tank treatments or other operations where excessive loss from volatilization is possible during the process. It should be a pure coal-tar creosote, consisting almost entirely of aromatic compounds. An oil of this sort is also particularly well adapted for use in processes where only a minimum quantity of the creosote is employed, such as an empty cell process, where

it is essential that nearly all of the oil used shall stay in the timber and protect it, since it is the sort of oil which would show a minimum loss by volatilization from treated timber.

Grade B is a pure coal-tar creosote, but contains a much larger proportion of the low boiling constituents than grade A. It is well adapted for closed cylinder operations and for timbers which will be protected by soil or water from excessive evaporation. .

Grade C allows a certain amount of added oil-tar creosote or products of a similar nature. The amount of aromatic compounds in the oil, however, would be so high that it ought to be fairly efficient as a timber preservative.

Grade D represents the poorest oils which can well be called creosotes and is not adapted for use with timbers where the maximum efficiency from impregnation is desired. Its use would be suggested for timbers where the cost of a high grade creosote might be undesirable.

Approved:

JAMES WILSON, *Secretary.*

WASHINGTON, D. C., *January 4, 1908.*

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